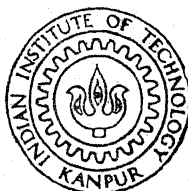


SEPARATION OF NORMAL PARAFFINS FROM PETROLEUM FRACTIONS BY MOLECULAR SIEVES

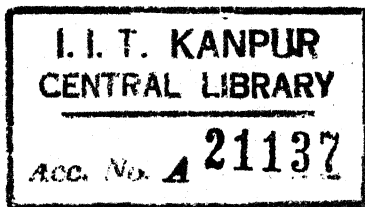
BY
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DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR
JUNE, 1972

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SEPARATION OF NORMAL PARAFFINS FROM PETROLEUM
FRACTIONS BY MOLECULAR SIEVES

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

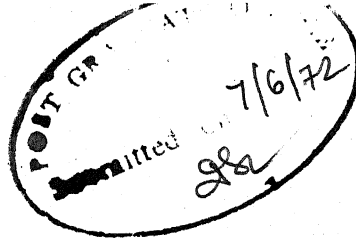
by

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to the

DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

JUNE, 1972



(ii)

CERTIFICATE

It is certified that this work has been carried out under my supervision and that this has not been submitted elsewhere for a degree.

Date: 6th June 1972

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<p>POST GRADUATE OFFICE This thesis has been approved for the award of the Degree of Master of Technology (M Tech.) in accordance with the regulations of the Indian Institute of Technology Kanpur Dated. <i>12/6/72</i></p>
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Author

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ABSTRACT

An equipment was constructed for separation of n-paraffins from different petroleum fractions from Naharkatia crude using molecular sieves. Effect of temperature was studied on adsorption of n-paraffins on molecular sieves. It was found that the time for equilibrium loading continuously decreased with increasing temperature although the amount adsorbed also decreased. The percentage recovery was found to be maximum at 150°C for naphtha 100°C for kerosine and 300°C for gas oil and was respectively 54%, 11% and 22%. The apparent high recovery in case of naphtha was thought to be due to n-olefins separating out along with n-paraffins. Out of the three desorbing fluids studied, liquified petroleum gas was found to be most suitable.

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CHAPTER I

INTRODUCTION

In modern chemical industries, normal paraffins are finding good scope. Normal paraffins in the C_{10} - C_{18} range carbon number, such as occur in kerosine and gas oil boiling range are required for the manufacture of synthetic detergents and plasticizers. These paraffins due to having highest heat of combustion can also be used as the fuel for aeronautic purposes. Low boiling n-paraffins are the raw materials for the production of acids, aldehydes and alcohols. Chlorinated waxes prepared from high molecular weight n-paraffins are lighter in colour and are more stable towards heat and ultraviolet light than the commercial chlorinated waxes produced by other methods.

Normal paraffins are undesirable in gasoline and particularly in aviation gasoline owing to their low octane rating. Therefore, extraction of these hydrocarbons can improve the anti knock characteristics of the gasoline at the same time providing a substantial source of n-paraffins. Other distillate fractions like kerosine and gas oil are also potential sources of these n-paraffins. It has been shown by Chandra et.al.⁽¹⁾ that a sizeable percentage of these hydrocarbons can be removed from kerosine without significantly altering the properties of denormalized stock.

The range of boiling points of n-paraffins overlaps with that of other hydrocarbons rendering fractional distillation a completely impractical method of separation. Urea Adduct Method was used to separate the n-paraffins in early days. This process has limitations in the sense that adduct formation is favored only for paraffins higher than C_5 . Also, as the carbon number increases, the consumption increases linearly⁽²⁾. Furthermore, urea is not very selective and even some non-normal paraffins can participate in adduct formation.

Barrer et.al.⁽³⁾ reported the selective adsorption of n-paraffins on natural zeolites (chabazite). Since then, crystalline zeolites are extensively used for separation and recovery of n-paraffins from the mixture of other hydrocarbons: In 1954, Linde Air Co., Division of Union Carbide Company, introduced synthetic zeolite calling "Molecular Sieves". Different types of molecular sieves are manufactured by them such as type 4A, 5A and 13X. Type 4A and 5A molecular sieves are characterized by a 3-dimensional structure or network having water of hydration. When water of hydration is removed, there remains an intracrystalline structure. The voids are forty-five volume percent of the zeolites. The size of the opening or voids depends upon the alkali metal of the zeolite. In case of 5A molecular sieve the alkali metal is calcium and the pore diameter is 5 Angstrom unit. These molecular sieves do not have the pore size distribution and this uniformity of pore size enables molecular sieves

to become selective in nature which results in sieving of the molecules. The mean cross sectional diameter of n-paraffin molecules is 4.9A where as iso-paraffins, cyclic molecules have minimum cross sectional diameter 5 to 6A. The naphthenes and aromatics have mean cross-sectional diameter greater than 6A. Thus under adsorptive conditions, if a mixture of various types of hydrocarbons ~~is~~ passed through a bed of Linde Molecular Sieve 5A (LMS 5A) the n-paraffins will be selectively adsorbed in the molecular sieve and the rest will be allowed to pass out. (21,22)

Based upon these observations, Universal Oil Product developed Molex Process in 1959 for improving the antiknock properties of gasoline on industrial scale. Afterwards, they extended the process for obtaining n-paraffins of detergent range^(4,5). UOP Molex process operates in liquid phase. It involves a number ^{of} fixed adsorbant beds in series provided with a programming device to change inlet and outlet points for various beds.

The desorption step where n-paraffin is recovered from the sieve bed is rather most tedious part of the process and this is the step where one process differs from the other. Molex process uses low boiling hydrocarbon for desorption of n-paraffins. The Isosiv Process of Linde Company operates on an isothermal pressure swing cycle. The adsorption is carried out in vapor phase and pressure swing cycle is used

to desorb n-paraffins at reduced pressure^(6,7). Initially, it extracted n-paraffins of C_5 - C_{15} range but later, it extended the process to separate the higher n-paraffins (C_{10} - C_{16}). The British Petroleum Molecular Sieve process was developed for the extraction of n-paraffins from gas oil⁽⁶⁾ (C_{10} to C_{18}). The adsorption is carried out in vapor phase and desorption is done with n-pentane purge. The Texaco Selective Finishing Process is employed to upgrade the octane number of catalytic reformat, light or even heavy straight run naphtha^(7,8,9,17,18). The Parex Process was developed by VEB Leuna Works "Walter Ulbricht", East Germany for production of C_{10} to C_{18} n-paraffins from petroleum fractions in the range 180° to 320°C in different stages⁽¹⁾. Firstly, they allow the n-paraffins to adsorb on a specially modified bed in presence of an auxiliary gas at 300 - 400°C and 5-15 atmospheric pressure. The temperature and pressure are maintained constant throughout the process. Secondly, a gas is used to remove material adsorbed in the secondary pore structure. At the end n-paraffins are desorbed with n-pentane.

Ashar, et.al.⁽¹⁰⁾ described a novel adsorption process - the Ensorb - process - developed by ESSO Research and Engineering Co. for the recovery of high purity n-paraffins using ammonia as desorbing agent. Paraffins upto C_{33} have been recovered by this process in pilot plant equipment. The process is operated at constant temperature (260 - 370°C) and constant pressure (15-50 psia). Adsorption takes place in vapor phase. By employing

the beds of adsorbent one in adsorption and one in desorption at all times, continuous flow of the feed and ammonia stream is maintained.

Present Study:

This study was undertaken with a view of developing a process for extracting n-paraffins from various petroleum distillates of indigenous origin. This should eventually lead to decreasing or even stopping the import of these hydrocarbons or their derivatives.

Straight run cuts of naphtha, kerosine and gas oil obtained from Barauni Oil Refinery processing Naharkatia (Assam) crude were taken for present study. The study includes the effect of increasing temperature on the equilibrium loading of the molecular sieves, on the volume recovery of n-paraffins and also on the volume percent recovery of n-paraffins.

The effect of different desorbing fluids, nitrogen, liquified petroleum gas (Indane) and carbon dioxide was also studied on the recovery of normal paraffins.

CHAPTER II

THEORETICAL CONSIDERATIONS

Adsorption of n-Paraffins:

The separation of normal paraffins from a given petroleum fraction is achieved by the selective adsorption of n-paraffins (adsorbate) on molecular sieves (adsorbent). The adsorption known as the Vander waals adsorption, involves forces of physical nature, such as the forces of attraction between solvent and adsorbate, adsorbent and adsorbate, and adsorbent and solvent.

The temperature and pressure (or concentration) are also very important in determination of the adsorption equilibrium. As the adsorption process is exothermic in nature, less material is adsorbed as the temperature is increased. The higher the pressure (or concentration), the more material will be adsorbed since the adsorption results in net reduction of volume of the hydrocarbon mixture.

The amount of the adsorbate adsorbed is a function of the final pressure or concentrations and the temperature

$$\frac{x}{m} = f(P, T)$$

Where, x/m = amount of material adsorbed/gm. of the adsorbent

P = Equilibrium pressure

T = Absolute temperature

When T is constant, the plot of x/m vs P is called isotherm.

Plot of x/m vs T is called Isobars where P is constant.

Plot of P vs T is called isostere, where amount adsorbed is constant.

Desorption:

The adsorption of n-paraffins on molecular sieve is favored by high equilibrium pressure and low temperature. In contrast, the desorption is done by raising the temperature of the bed or by some means reducing the equilibrium pressure of the adsorbate on the molecular sieve bed. Reduction in partial pressure is done by purging some other gas like N_2 or low boiling n-paraffins. Instead passing non-polar purge gas, if a polar gas is passed, it reduces the equilibrium partial pressure and also displaces the n-paraffins adsorbed in the molecular sieve bed. At elevated temperature, if a polar gas like ammonia, CO is passed, the desorption time taken will be the least of all⁽¹¹⁾.

(a) Desorption is achieved by elevating the temperature of molecular sieve bed (thermal swing cycle). Desorption temperature should be high enough to keep the desorbed n-paraffins in vaporized state for recovery. This method is suitable for low boiling fractions because high boiling fractions of n-paraffins may undergo cracking⁽¹¹⁾.

(b) Reduction in partial pressure is done by performing desorption under vacuum (Pressure swing cycle). But adsorbed high molecular weight n-paraffins are almost

insensitive towards reduction of pressure hence desired result may not be obtained⁽¹¹⁾.

- (c) Desorption by sweeping with a non-adsorbable material (Purging).-- Sweeping the loaded molecular sieve bed with some non-adsorbable gas, such as N_2 the desorption mechanism becomes essentially as in pressure swing cycle. By continuously sweeping the n-paraffins from sieve bed as they are desorbed, the partial pressure of the n-paraffins in the atmosphere surrounding the sieve bed is kept below that of the n-paraffin adsorbed on the molecular sieve. Due to this phenomena, the transfer of n-paraffins continues in order to reach equilibrium. This method is essentially same as the pressure swing cycle, more suited for low boiling or low molecular weight n-paraffins⁽¹¹⁾.
- (d) Displacement desorption using an adsorbable material which is more strongly adsorbed than the material being desorbed: The fact that molecular sieves have more adsorption affinity for higher molecular weight n-paraffins than for lower molecular weight n-paraffins, the desorption of n-paraffins can be done by a desorbing media of higher molecular weight n-paraffins than the desired. Excellent results can be obtained but the method is subject to criticism due to lowering the efficiency of molecular sieve bed in subsequent adsorption step. The n-paraffins in charge stock will not readily displace the n-paraffins more strongly adsorbed desorbing medium n-paraffins.

Instead of using high molecular weight n-paraffins, if some polar gas like ammonia or carbon dioxide is used, the molecular sieve will prefer the polar compounds for adsorption releasing adsorbed n-paraffins. Excellent results have been obtained by ESSO Research and Engineering Co.⁽¹⁰⁾.

(e) Displacement desorption using low boiling n-paraffins. This technique involves two primary driving forces. Firstly, the sweeping effect of the desorbing medium flowing through the sieve bed causes the desorption in the same manner as in the sweeping with nonadsorbable material and secondly, the normal paraffin in desorbing medium, though less strongly adsorbed than the n-paraffins on the sieve bed, are present in large excess during the desorption step and tend to be adsorbed, displacing the product n-paraffins from sieve bed. Since, the adsorbed low boiling desorbing medium can be easily displaced by the n-paraffins in the feed (it will complete one operating cycle.)

In this case the sieve bed is loaded with n-paraffins of either low molecular weight or high molecular weight in the beginning of adsorption or desorption step. During both steps n-paraffins are being adsorbed and desorbed, the effect of heat of adsorption and desorption is negligible. This is because of the fact that while the adsorption is exothermic, the desorption is endothermic. Another key feature of desorption using a lower molecular weight n-paraffins desorbing medium is the small effect

of pressure variations on desorption rate. Reduction of pressure tends to reduce the loading of the product n-paraffins on the sieve, but it also impedes adsorption of the n-paraffin from desorbing medium. Since adsorption of these desorbing medium n-paraffins supplies part of the desorption driving force, the overall effect of pressure variation on desorption is normally small.

CHAPTER III

EXPERIMENTAL SETUP

A schematic diagram of the equipment used is shown in Fig.1.

Adsorption Column: It consisted of 26" long 1" O.D. ($7/8$ " I.D.) stainless steel tube fitted with caps on both ends. To these caps were attached 6" long and $1/4$ " O.D. ($1/8$ " I.D.) stainless steel tubing on both ends. Both top and bottom connections bifurcated in two lines, one from each going through the preheater and the rest two to condensers. A $1/4$ " stainless steel needle valve was placed on each line immediately after bifurcation. The tube was packed with 250 gms. of LMS 5A molecular sieves which were in the form of $1/16$ " pellets. In order to prevent the chocking of flow line in the bottom adsorber a wire gauge was placed between the cap and the adsorber. Another wire gauge was placed in the similar fashion at the top to work as a distributor for the feed. The column fitted with connections was inserted to a tubular furnace of $2\frac{1}{4}$ " I.D. and 32" long held in vertical positions.

Furnace/Heater: The furnace or the heater used to raise the temperature of the adsorption column was made from a silliminite tube of $2\frac{1}{4}$ " I.D. and 32" long. Since the length was too long to have a uniform temperature distribution it was decided to divide the furnace in two sections provided with two different temperature

controllers. Both sections were wound with 16 gauge nichrome wire each having approximately 8 ohms resistance. The thermocouples for both the controllers were suspended 11" and 24" respectively, from the top. The temperature was controlled within $\pm 2^{\circ}\text{C}$ in both sections. The variation in temperature along the length of the furnace in the zone of interest was not more than 5°C . This was checked in the following manner:

The furnace temperature was controlled at 100° , 200° , 400° and 500°C separately. Chromel-alumel thermocouple was inserted to the bottom of the furnace. It was then lifted at 2" interval upward and corresponding temperature was recorded with the help of a potentiometer. In all the cases it was found that there was a temperature variation of $4-5^{\circ}\text{C}$ in the zone in which the adsorption column was housed.

Preheater: The temperature of preheater was controlled manually with help of a pyrometer and a variac. It was a Lindeberg furnace type - 54241.

Flowmeter: To measure the flow rate of the feed to the adsorption column, a precision rotameter made by F.W. Dwyer Manufacturing Co., 1 to 5 liter of air per minute capacity was used. Appropriate calibration was done for different feeds.

Sampling and Collection:

The effluent from the bottom of adsorption column was collected at the 1 minute interval in test tubes. Normal paraffins from the top of the adsorption column were collected in the

measuring cylinder.

Materials Used:

The following petroleum distillates were used:

Distillate	Boiling Range
Straight run naphtha	100°C to 130°C
Straight run kerosine	140°C to 300°C
Straight run gas oil	270°C to 350°C

These were obtained from Barauni Refinery which processes Naharkatia (Assam) crude.

CHAPTER IV

EXPERIMENTAL PROCEDURE

The experimental set-up is shown in a schematic diagram Fig.1. The petroleum fraction (naphtha, kerosine etc.) was placed in the feed tank located at a height of about 6-8 ft. from which the hydrocarbon was allowed to flow undergravity. The flow rate was controlled through a needle valve (V_2) and measured with a rotameter placed in the line. The hydrocarbon was then allowed to pass through the preheater which was a straight stainless steel tubing 24" length and 1/4" diameter placed in a controlled temperature furnace. The heated feed was allowed to enter the adsorption column maintained at the temperature same as in preheater section. The effluent stream was cooled and collected. After the adsorption was complete the feed was switched off. The adsorbed n-paraffins were subsequently desorbed.

Calibration of Rotameter:

The viscosity of the hydrocarbon used was so widely different that it became necessary to calibrate the rotameter for each fraction separately. Moreover, the particular rotameter used was an air rotameter. The valves V_1 and V_3 were opened. Operating the valve V_2 of the rotameter, the float was controlled at 5 litres per minute (LPM) mark and liquid coming out of valve V_3 -just before the entrance to the adsorption column, was collected in a measuring cylinder for a known interval of time.

recorded by a stop watch. This was repeated thrice and average was taken as the flow rate. The same was repeated at other graduations on the rotameter and a calibration curve was prepared for each of the fluids used (Appendix A).

Leak Test: The equipment was tested against leaks at 20 psig and was found to be free of leaks.

Activation of the Molecular Sieves:

The furnace temperature was raised upto 400°C which in turn raised the temperature of the sieve column to 400°C. After about one hour nitrogen gas at 5 psig preheated to 400°C in the preheater was allowed to pass through the column. This flushed the column of any previously adsorbed impurities and moisture on the molecular sieves. After half an hour the nitrogen supply was cut off and the column was allowed to cool. It was then ready for use.

Adsorption:

The sieve column was activated as described above. Its temperature was raised to a level at which adsorption was to be carried. The temperature of the preheater was also raised to the same level. Naphtha was taken in the feed tank and was allowed to flow through the preheater. The flow rate was controlled by valve V_2 and measured with the help of rotameter. The feed from the preheater section was fed to the adsorption column from the top. During this period valves V_5 and V_6 remained closed. The effluent after adsorption coming out from the bottom was allowed to pass through the condenser C1. This stream was

completely devoid of n-paraffins in the beginning of the run, but after break-through occurred n-paraffins also started coming along the stream. After the equilibrium was reached, the adsorption process was stopped by closing the feed valve V_1 . To ascertain the equilibrium point, small samples of the effluent were collected in test tubes after every one minute. Refractive index was monitored for these samples (data given in plots in Appendix) on an Abbe Refractometer. An S-shaped curve was obtained, levelling off of the curve marked the equilibrium. This was also checked for one adsorption run at room temperature for naphtha and two adsorption runs at room temperature and 100°C for kerosine by using chromatographic analysis. ^(19,20) (Chromatograph used was varian associates, Aerograph model, column used for naphtha was S-E-30, silicon gum rubber coated on chromosorb-P, column used for kerosine: Apiezon-L coated chromosorb-P.). The equilibrium points indicated for these runs, by levelling off of the peak heights of n-paraffins on the chromatograms were in conformity with the ones obtained by refractive index analysis. Therefore for the rest of the runs only refractive index data were used.

Before desorption process was started to unload the molecular sieve, it was necessary to remove the feed present in the flow lines. This was done by blowing very low pressure nitrogen through the system.

Similar procedure was adopted for adsorption of n-paraffins from kerosine and gas oil.

Desorption:

The n-paraffins adsorbed on the molecular sieves were desorbed by sweeping the column with different desorption gases like nitrogen, LPG (Indane), carbon dioxide. The column temperature was raised to 200°C in case of naphtha and kerosine and 300°C in case of gas oil, since gas oil has high molecular weight n-paraffins. Preheater temperature was also raised to similar level. The purge gas was then turned on, preheated and passed through the bottom of the adsorption column. Valves V_3 and V_4 remained closed and V_5 and V_6 remained open during this operation. Desorbed n-paraffins were removed along the purge gas through V_6 which passed through the condenser C_2 and were collected in a measuring cylinder after condensation. The purge gas was allowed to escape in the atmosphere. Desorption process was continued untill all the adsorbed n-paraffins were recovered.

Normal Paraffin Recovery by Urea Adduction Method:

Urea selectively crystallizes around organic compounds with long straight chains to make a solid, filterable complex or adduct. This selectivity of adduct formation is a function of the cross-section of the organic molecules as related to the geometry of the urea crystal. In forming the adduct, the urea crystal forms a channel large enough to accommodate straight chain hydrocarbon molecules like n-octane, but not cyclic or branched-chain hydrocarbons like benzene or isoparaffins.⁽¹²⁾

Around 0.7 moles of urea is needed to form an adduct with each carbon atoms. Also the molecular weight of hydrocarbons is almost proportional to the number of carbon atoms, the ratio on a weight basis is almost constant - roughly 3 lbs of urea for one pound of hydrocarbons.⁽¹²⁾

Petroleum fractions having low content n-paraffins can be dewaxed with urea only. Whereas, if the content of these n-paraffins is appreciable, it is found that the mixture of the oil and the urea, dissolved in it, thickens very rapidly to a heavy paste even under stirring conditions. It becomes difficult to filter or pump this paste. Hence, these stocks are diluted with some solvent before adduction is carried out. Methylene chloride is preferred to other solvents such as methanol for adduct-formation. It's boiling point of 41°C lies in the range 36 to 45°C most suited for adduct formation. Heat liberated by adduct formation is

carried out by the vaporization of a portion of the solvent without any serious temperature variation. It is non-corrosive and non-inflammable.⁽¹³⁾ Urea is also dissolved in a solvent, usually water⁽¹³⁾, so that intimate mixing of hydrocarbons with urea can be achieved

Experimental Procedure:

A charge of 100 cc of naphtha, kerosine or gas oil, was kept in a reaction vessel of 1 litre capacity fitted with stirrer. This vessel was placed in a constant temperature bath. To this 100 cc of methylene chloride was added and thoroughly mixed, 100 cc of saturated aqueous solution of urea at 70°C was added and thoroughly mixed. The temperature of the bath was maintained at 40°C. The adduct formation took place in a few minutes. The adduct was then filtered. To the filtrate, water at 40°C was added which readily dissolved the adduct. The solution was transferred to a separating funnel where n-paraffins get separated from urea solution. The n-paraffins obtained was collected in a measuring cylinder and the amount was noted down.

Results:

	Run No.	Volume treated, cc	n-paraffin collected, cc	Vol. %	Average
Naphtha	1	100	4	4	= 4
	2	200	7	3.5	
Kerosine	1	100	8	8	= 7
	2	100	6	6	
Gas oil	1	100	11	11	= 12
	2	100	12.5	12.5	

Density of naphtha 0.71940 gm/cc

Density of n-paraffins of
Naphtha boiling range 0.8445 gm/cc

Density of kerosine 0.81745 gm/cc

Density of n-paraffins of
Kerosine boiling range 0.9259 gm/cc

Density of gas oil 0.8200 gm/cc

Density of n-paraffins of
gas oil boiling range 0.8898 gm/cc

CHAPTER V

RESULTS AND DISCUSSION

Three straight run petroleum fractions, naphtha (boiling range: 100 to 130°C), kerosine (140 to 300°C) and gas oil (270 to 350°C) obtained from Barauni Refinery were used in the present study. The effect of temperature was studied on equilibrium loading of n-paraffins on molecular sieves (LMS5A) at atmospheric pressure and the data are presented in Fig.2. These data are plotted as grams of n-paraffins recovered per 100 gms of molecular sieve (dry basis) as function of temperature for different desorption fluids used. In all the three cases of naphtha, kerosine and gas oil, the equilibrium loading was found to decrease linearly with temperature rise. This is to be expected in view of the fact that adsorption decreases as temperature increases. The maximum loading was found to be around 17%, 30% and 26% for naphtha, kerosine and gas oil respectively at room temperature (20°C) which was the lowest temperature used in this study. Cooper et.al.⁽¹¹⁾ have reported similar findings for naphtha. For naphtha and kerosine the set of data using nitrogen as purge gas were repeated to ensure the producibility of data. As is clear from the figure both runs gave results well within experimental uncertainty.

The percentage recovery of n-paraffins (defined as volume of n-paraffins recovered divided by total volume of hydrocarbon

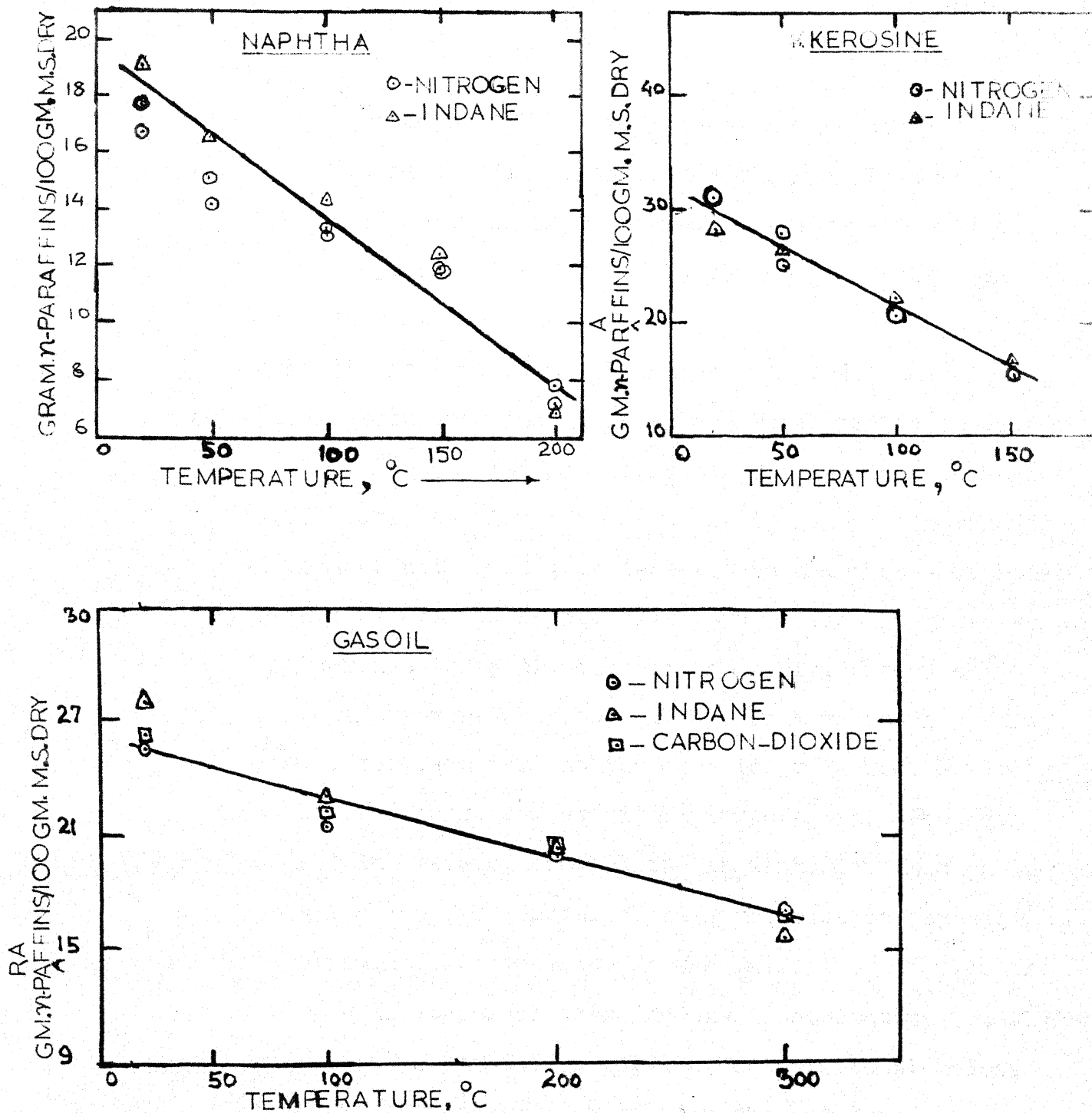


FIG 2. EQUILIBRIUM LOADING AS FUNCTION OF TEMPERATURE

treated and multiplied by 100) is plotted as a function of temperature on figure 3. Also included on the same figure is the total amount of n-paraffins recovered in a single run (i.e. total amount of n-paraffins separated by 250 gms. of molecular sieve) for comparison.

Looking at the plot of total volume of n-paraffins recovered, it is seen that amount of volume recovered decreased in every case as the temperature was raised similar to observation made in Fig.2. But, the plot of percentage recovery of n-paraffins showed an increased upto a certain temperature and then a decrease when temperature was raised beyond that point. Though, there was a continuous decrease in total volume of n-paraffins recovered in every case with temperature rise, the percent volume recovered increased due to the fact that at the same inlet flow, the time to reach equilibrium decreased at higher temperature. The main process involved in reaching equilibrium is diffusion through the solids. The diffusion rate increases with the rise in temperature. The point of maximum is reached due to the fact, that though, the rate of diffusion is increased with increased temperature, resulting in decrease in time to attain equilibrium, but the total volume adsorbed decreases substantially rendering the net decrease in the percent volume recovered. This means that the efficiency of the column to separate n-paraffins increased with temperature rise in the beginning. It reached a maximum and then started decreasing again.

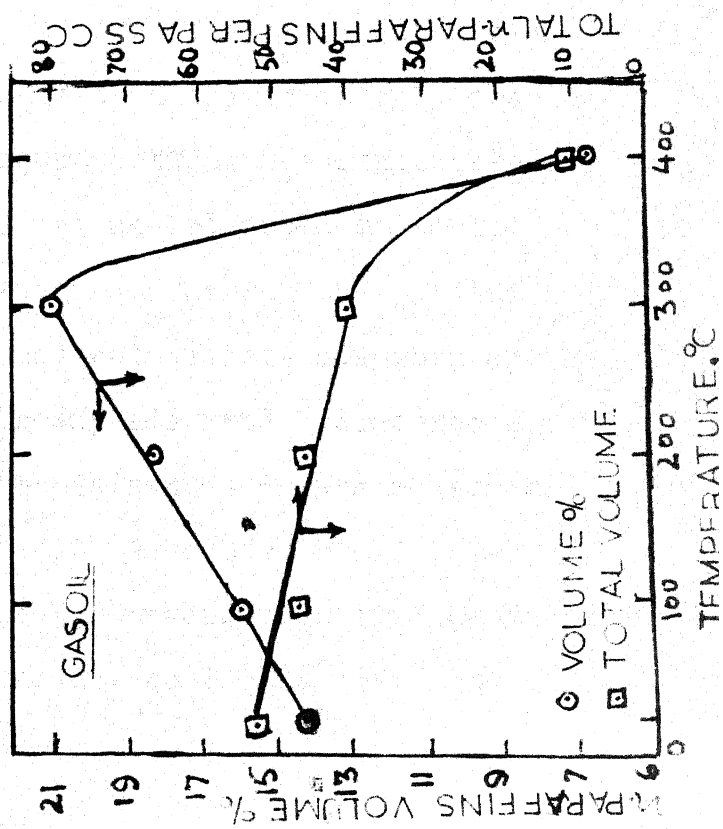
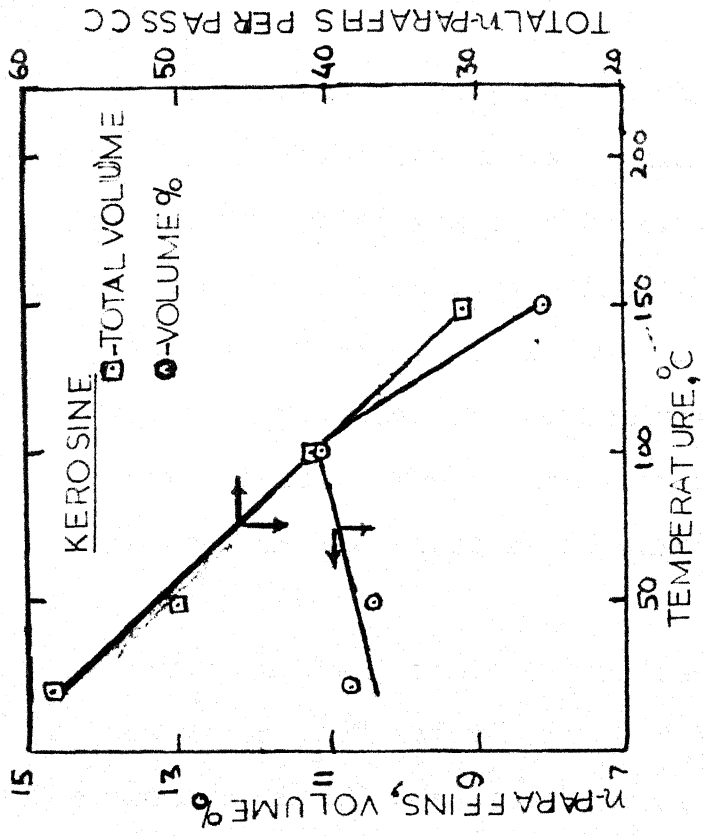
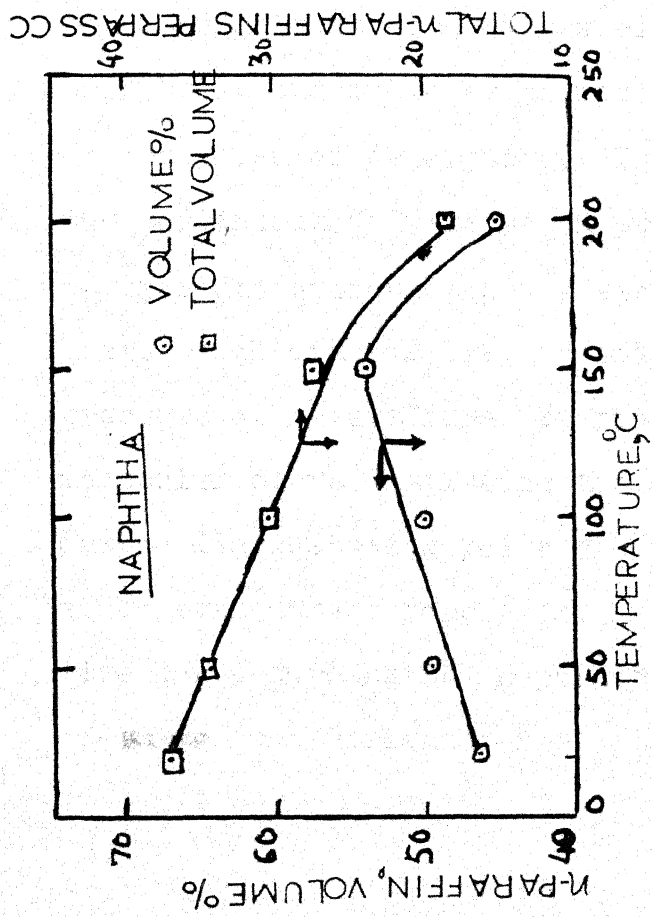


FIG 3. PERCENT VOLUME & TOTAL VOLUME OF PER PASS OF n-PARAFFINS AS FUNCTION OF TEMPERATURE

The desorption temperature was kept constant at 200°C in case of naphtha and kerosine and 300°C for gas oil. The effect of desorbing gas such as nitrogen, L.P.G. (Indane) and carbon dioxide on desorption time was studied. The data is presented in Figs. 4. In this figure the desorption time is plotted as a function of temperature of adsorption for different desorption gases. The pressure of nitrogen and LPG was always 5 psig whereas the pressure of carbon dioxide was kept at 2 psig.

From figure 4 it is clear that nitrogen as a desorbing gas was quite inefficient and took excessively long time. Performance of LPG was far superior to that of nitrogen, cutting down the desorption time significantly. Carbon dioxide, which was used only in case of gas oil, had the least desorption time. This behaviour is to be expected in view of earlier discussions on mechanism of desorption. In case of nitrogen it only creates the continuous difference in pressure between the atmosphere of n-paraffins surrounding the sieve bed and adsorbed molecules where as in case of LPG, in addition to lowering the partial pressure of n-paraffins, propane and butane gets adsorbed on the molecular sieve displacing the already adsorbed hydrocarbons. (23) Carbon dioxide having polar $C=O$ bond adsorbes on the molecular sieve even more strongly and hence it takes even still lower time for desorbing the n-paraffins. However, this strong affinity of ~~the~~ carbon dioxide has a disadvantage in the sense that

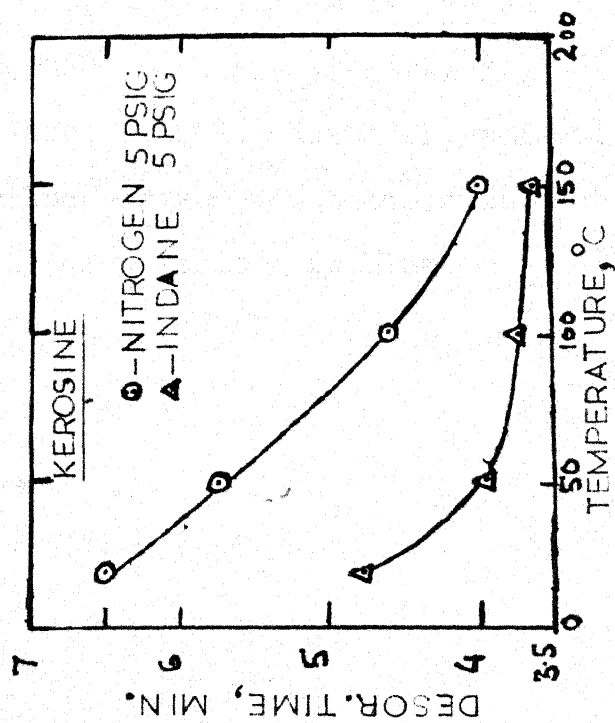
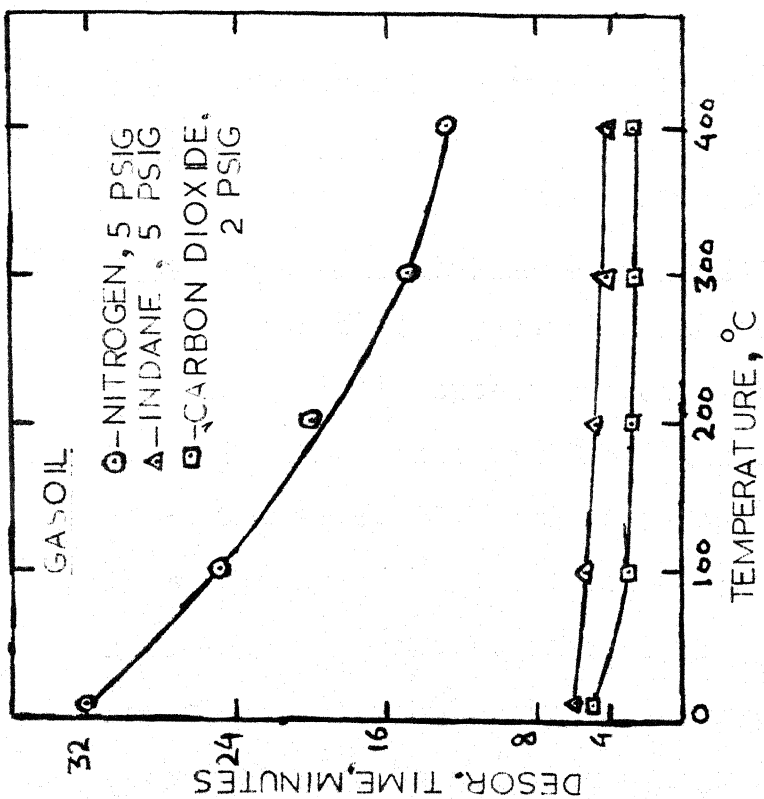
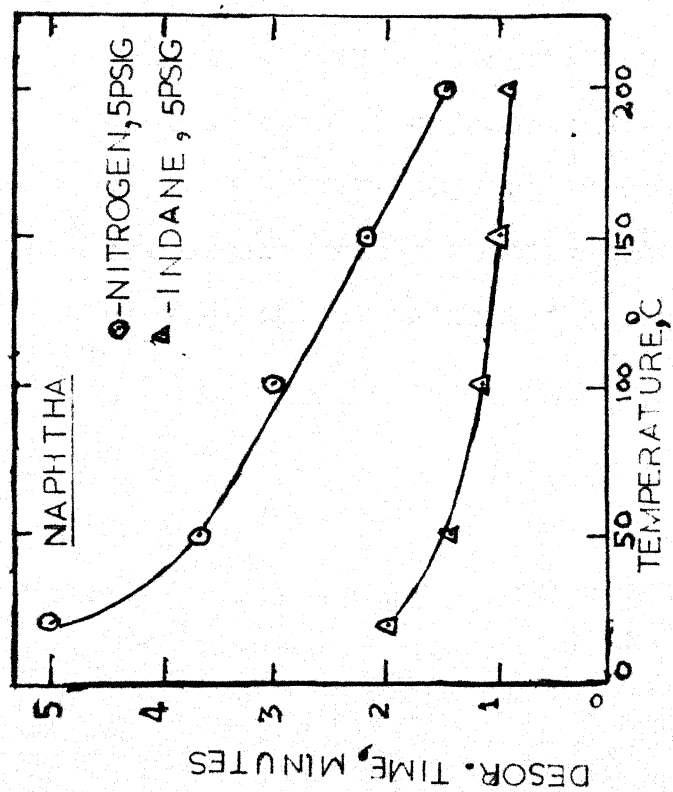


FIG 4. DESORPTION TIME AS A FUNCTION OF ADSORPTION TEMPERATURE

the bed becomes less adsorbent for n-paraffins in subsequent adsorption cycles.

Comparison of Molecular Sieve Method with Urea Adduct Method:

Amounts of n-paraffins recovered by urea adduct method were 4, 7 and 12 percent respectively for naphtha, kerosine and gas oil. The corresponding figures for molecular sieve method of 20°C are 46, 10.5 and 14 percent. At the optimum temperatures these figures are 54, 11 and 22 percent respectively for naphtha, kerosine and gas oil. The figure of 46 percent (or 54%) for naphtha is obviously very high. This may be attributed to the fact that naphtha contains a high percentage of n-olefins which have comparable molecular size and as such gets retained in the molecular sieves along with n-paraffins. Otherwise, it is seen that in case of molecular sieve method, recovery of n-paraffins is much better compared to urea adduct method. Moreover, molecular sieves are easily reactivated for successive runs whereas in case of urea adduct method, the recovery of urea is a problem.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Conclusion:

1. As the adsorption temperature was increased, the time for equilibrium loading of n-paraffins on molecular sieves decreased.
2. With increasing temperature, the total amount of n-paraffins adsorbed on the sieves decreased, but the percent volume recovery increased upto a certain temperature and finally started decreasing. The existence of optimum adsorption temperature was thus indicated for each petroleum fraction studied.
3. Of the three desorbing fluids used, liquified petroleum gas (Indane) seemed to have best promise.
4. A comparison of results obtained by molecular sieve method with those obtained by urea adduct method showed that the former gave higher yield of n-paraffins. Urea adduct method may also prove to be less economical.

Recommendation:

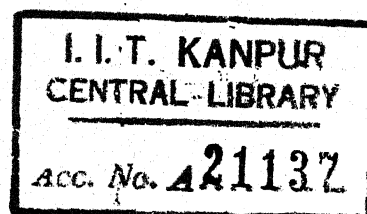
In the present study petroleum fractions were obtained from Naharkatia crude which has a very poor n-paraffin content. It is desirable that such a study be undertaken using other crudes preferably from western region. Ankaleshwar crudes are known to contain upto 40 percent n-paraffins. The potential for commercial exploitation lies only in those crudes.

A chromatographic analysis of the n-paraffins recovered will reveal the composition in terms of carbon number distribution which is important in deciding its use. This, however, would need standard samples of n-paraffins.

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APPENDICES

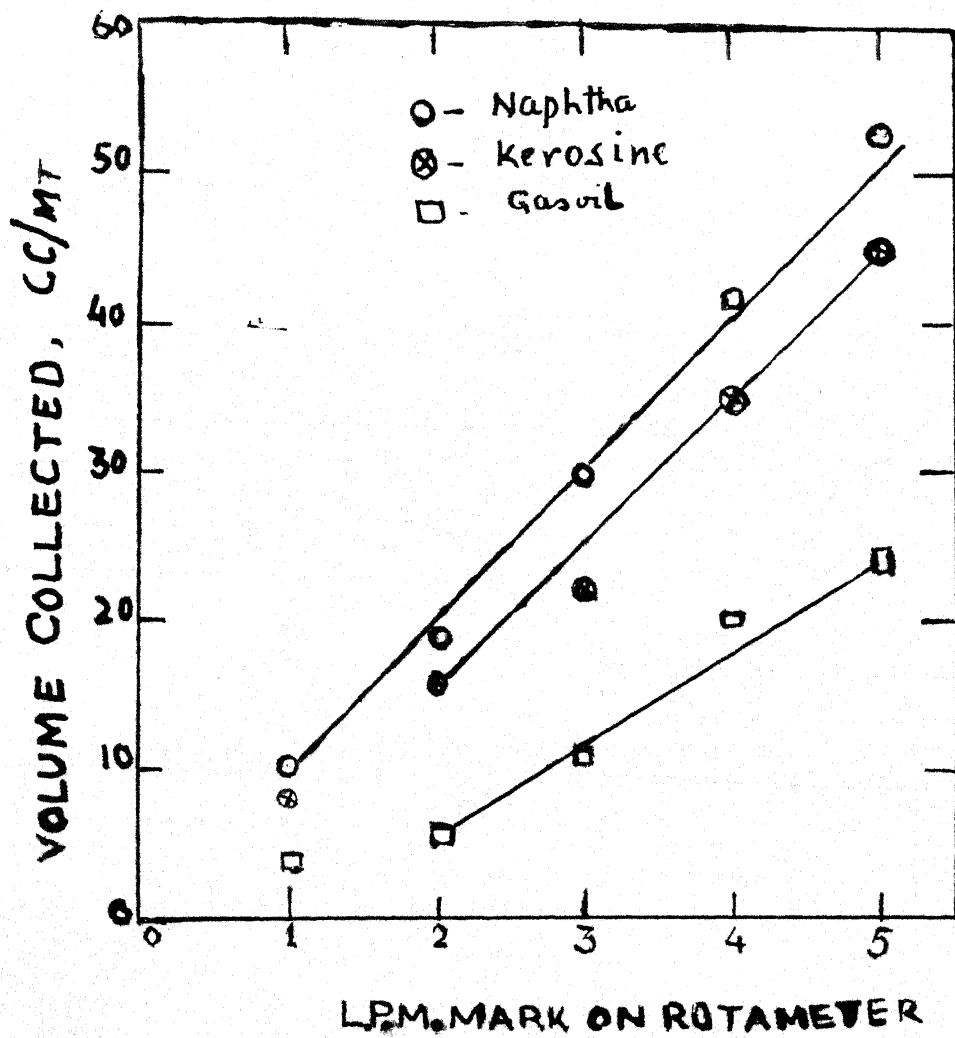


FIG. A1 CALIBRATION OF ROTAMETER

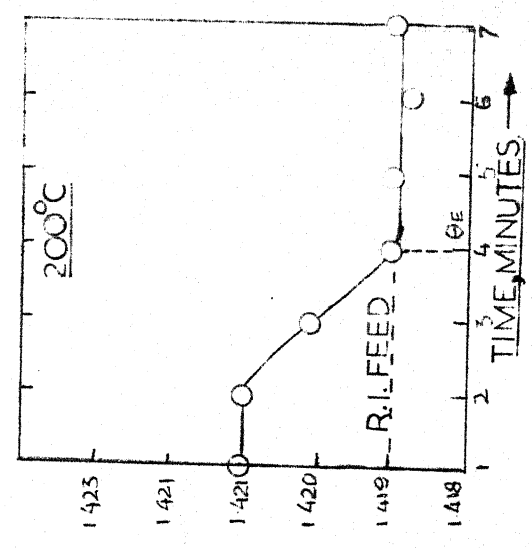
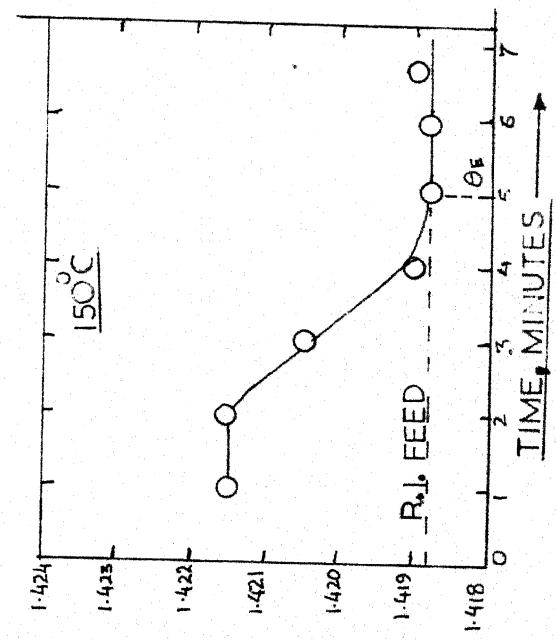
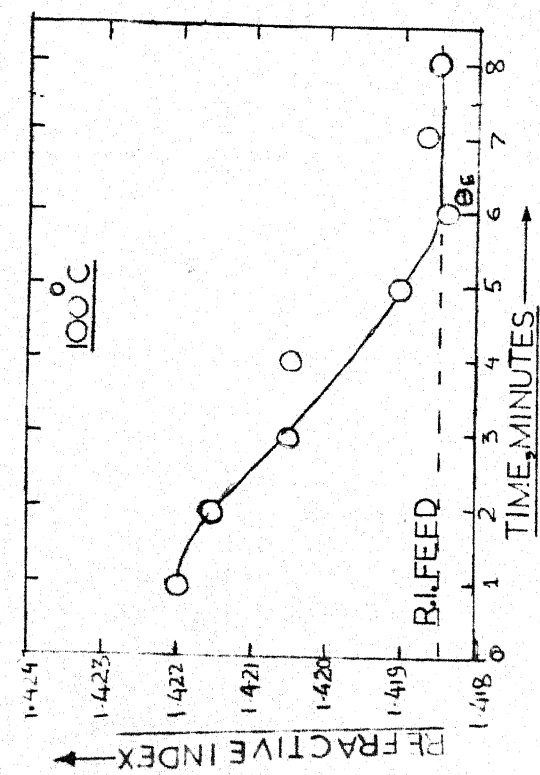
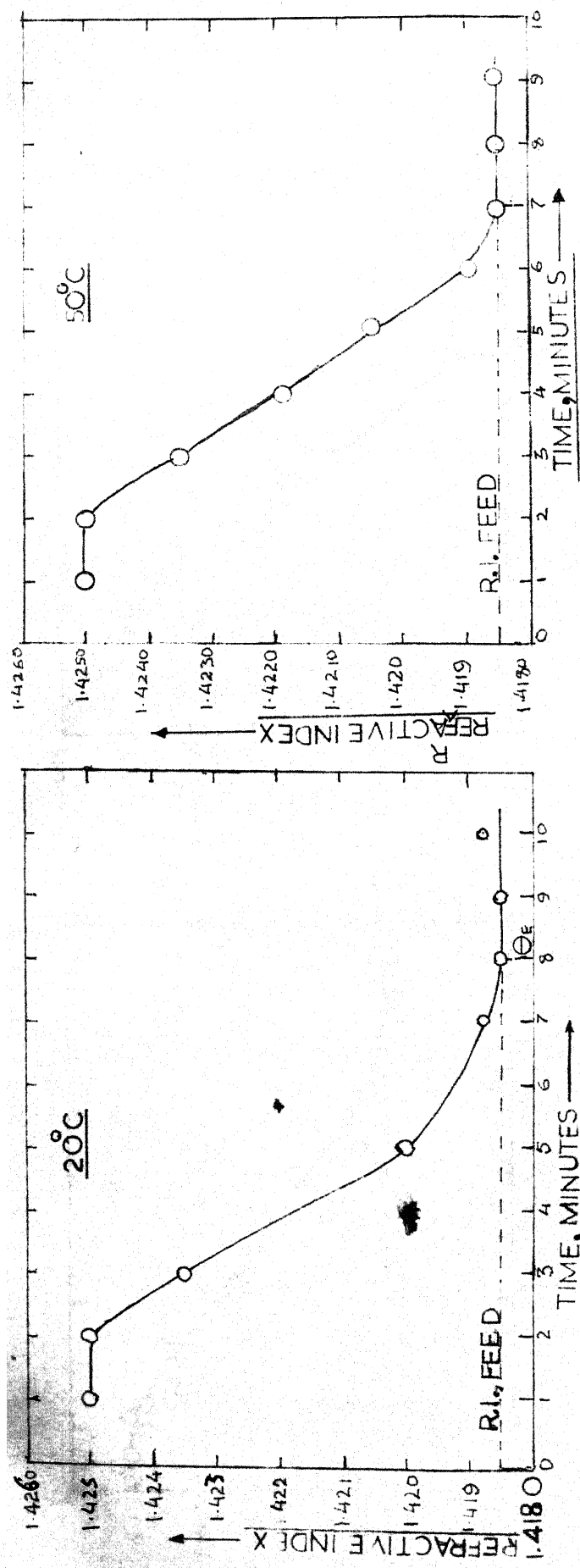
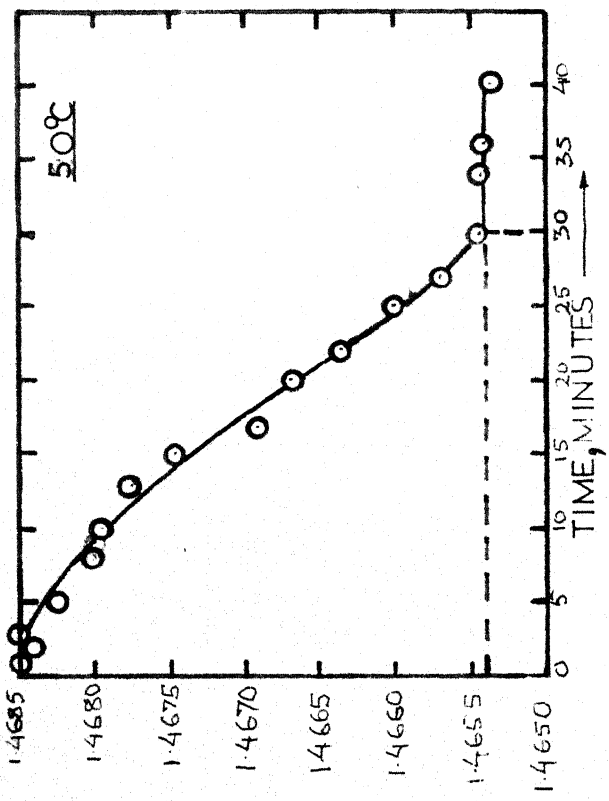
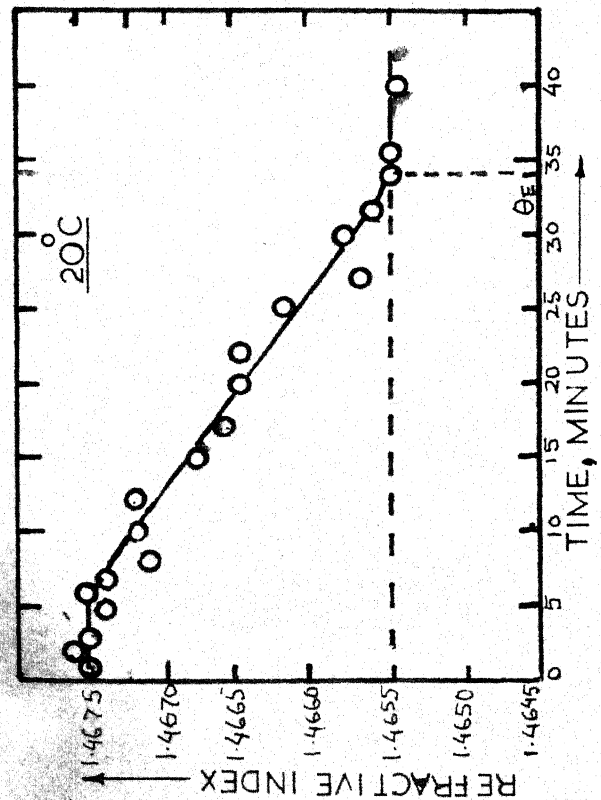
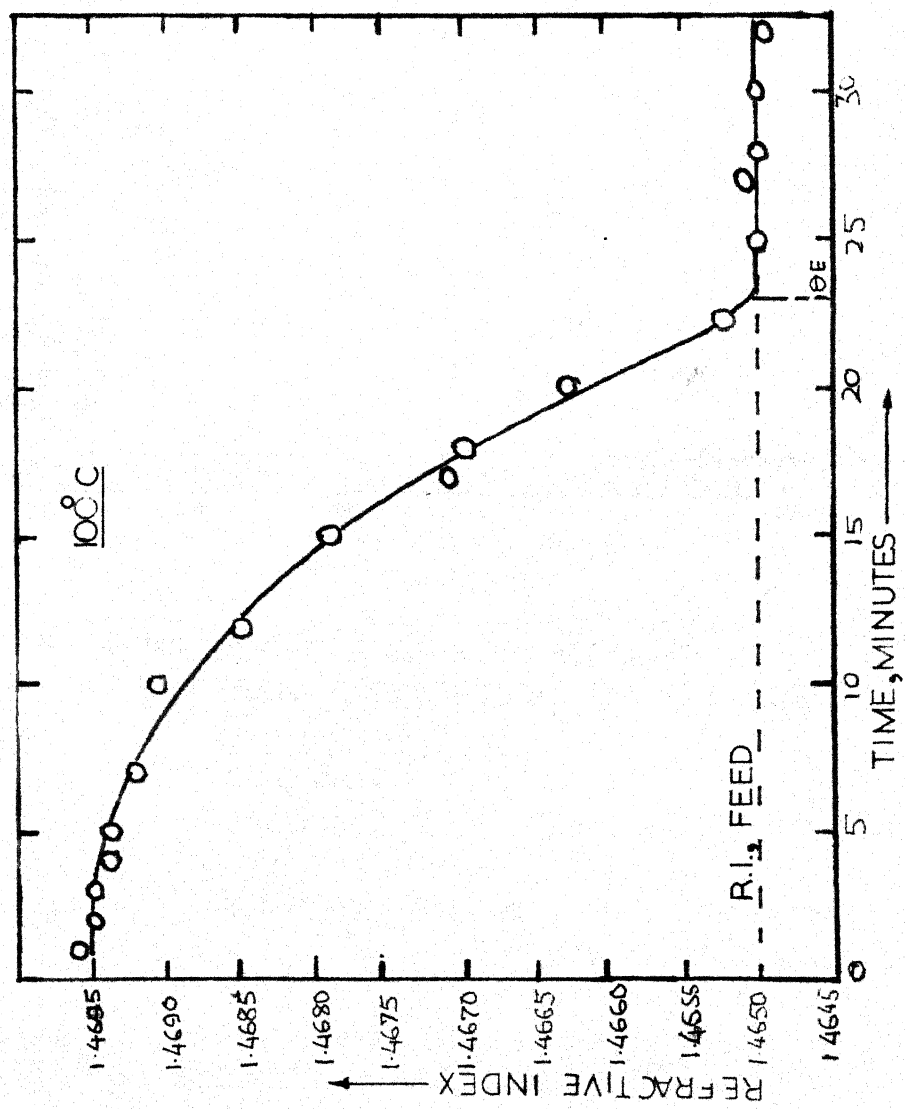


FIG. A2. BREAKTHROUGH CURVES FOR NAPHTHA AT DIFFERENT ADSORPTION TEMPERATURES



CONTD-----



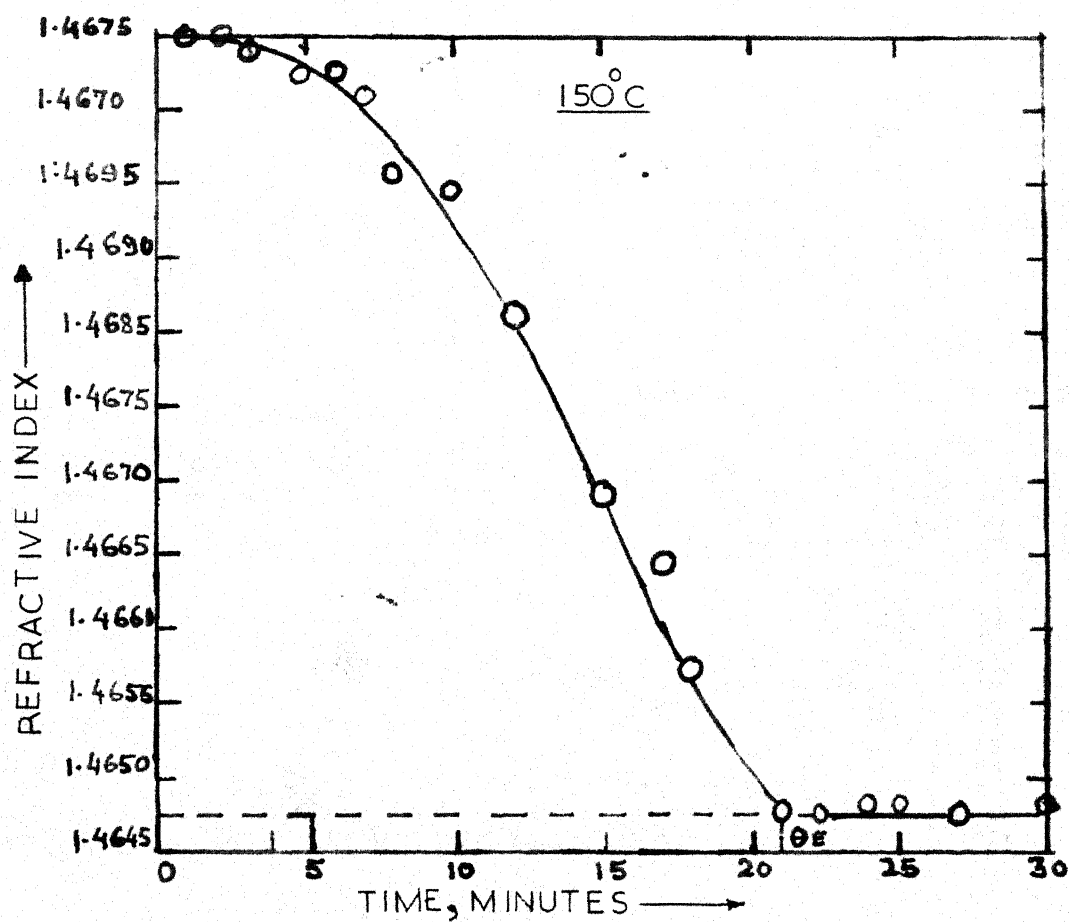


FIG A3. BREAKTHROUGH CURVES FOR Kerosine AT DIFFERENT ADSORPTION TEMPERATURES

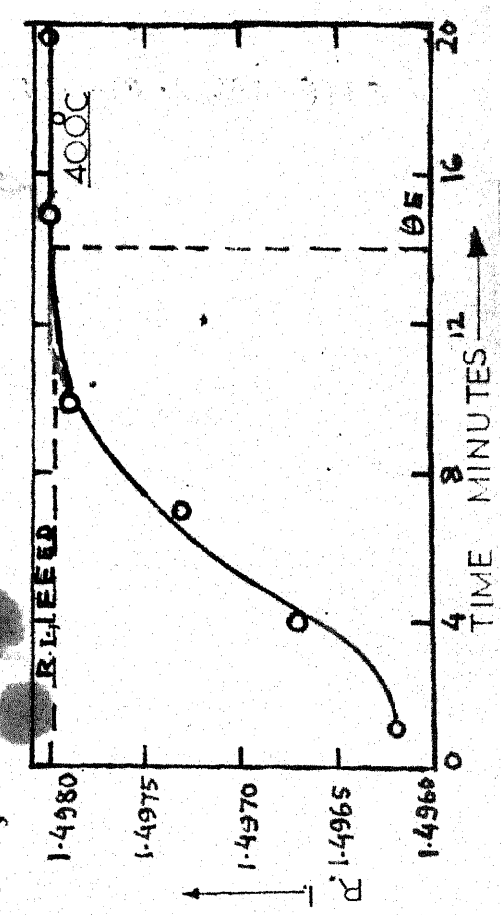
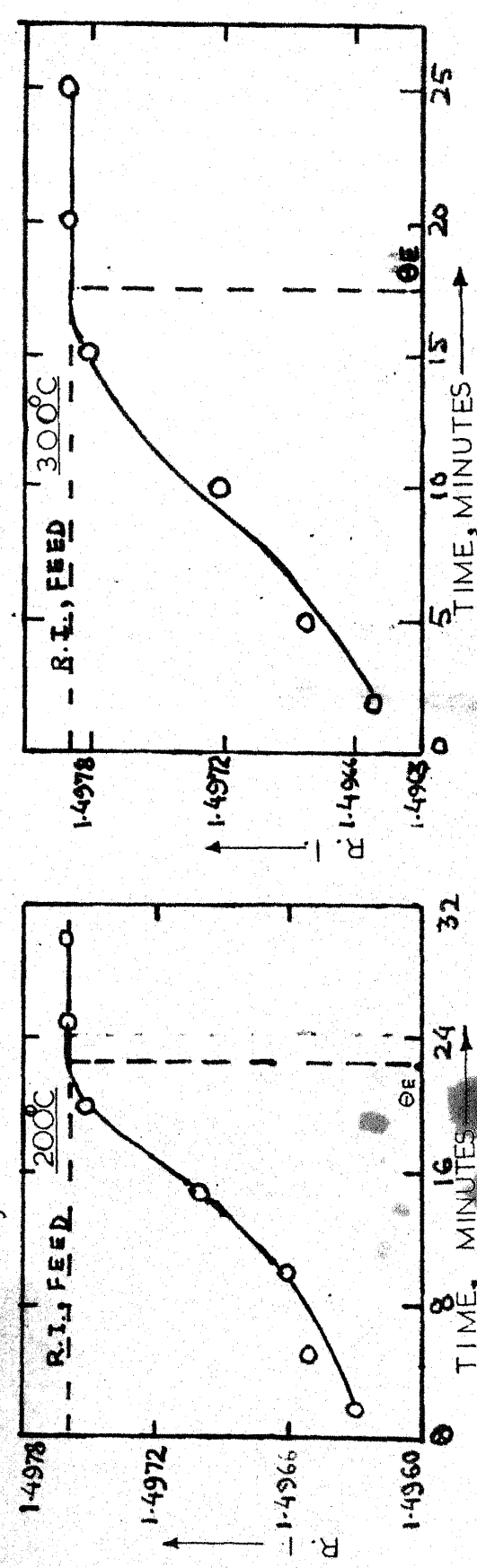
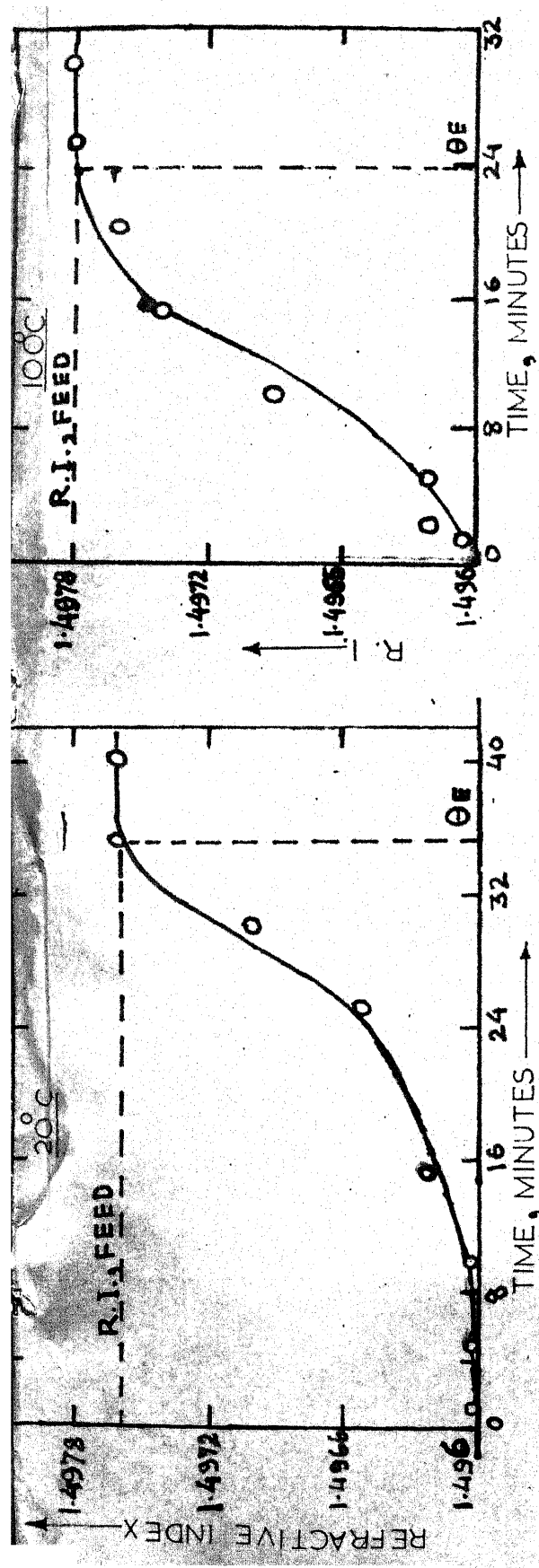


FIG. A4. BREAKTHROUGH CURVES FOR GAS OIL AT DIFFERENT ADSORPTION TEMPERATURES